



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

0 285 834
A1

GB

(2)

EUROPEAN PATENT APPLICATION

(1) Application number: 88103673.5

(5) Int. Cl. C07C 165/00, C30B 25/02,
C30B 29/48, C23C 16/18

(3) Date of filing: 09.03.88

(3) Priority: 07.04.87 US 35329

(7) Applicant: AMERICAN CYANAMID COMPANY
1937 West Main Street P.O. Box 60
Stamford Connecticut 06904-0060(US)

(4) Date of publication of application:
12.10.88 Bulletin 88/41

(7) Inventor: Valentine, Donald, Jr.
20 Blue Ridge
Ridgefield Connecticut 06877(US)
Inventor: Brown, Duncan William
30 Cobblestone Place
Wilton Connecticut 06897(US)

(5) Designated Contracting States:
BE CH DE FR GB IT LI NL SE

(7) Representative: Wächtershäuser, Günter, Dr.
Tal 29
D-8000 München 2(DE)

(54) Allyltellurides and their use in the MOCVD growth of group II-VI epitaxial films.

(57) Methyl allyltelluride is described for use in a process for depositing group II-VI epitaxial films in semiconductor manufacture. The films are grown on crystalline substrates in a MOCVD reactor.

EP 0 285 834 A1

ALLYLTELLURIDES AND THEIR USE IN THE MOCVD GROWTH OF GROUP II-VI EPITAXIAL FILMS

The invention relates to novel tellurium compounds and their use in improved processes for making semiconductor materials comprising epitaxial growth of group II-VI semiconductor compounds.

A most useful application for semiconductor materials of group II-VI elements is the manufacture of infrared detector devices. Of special importance in this area is the preparation of epitaxial films containing cadmium, mercury and tellurium deposited on semiconductor substrates. Specific compounds that may be grown epitaxially include cadmium telluride (CdTe), mercury telluride, (HgTe) and cadmium mercury telluride (CdHgTe). Several methods have been used for the growth of epitaxial films including liquid phase epitaxy, molecular beam epitaxy, elemental vapor phase transport, and metal-organic chemical vapor deposition (MOCVD). The latter, also known as organometallic vapor phase epitaxy (OMVPE) is a most convenient and practical method for the production of high quality epitaxial films. However, this technique has not been quite successful in the case of mercury, cadmium tellurium compounds, such as for example HgCdTe. In the preparation of this material, vapors of dimethylcadmium and diethyltelluride are introduced into an MOCVD reactor and mixed with mercury vapor which is generated by heating elemental mercury. The above vapor mixture in a stream of hydrogen carrier gas is allowed to chemically interact on the surface of a crystalline substrate, such as for example CdTe, to form an epitaxial film of HgCdTe. There are several problems with this method. First, the high temperature (greater than 400°C) required to decompose the diethyltelluride causes interdiffusion of high vapor pressure metals, such as mercury, at crystal interfaces thus resulting in poor quality product. Another important detrimental effect is condensation of excess mercury vapor on the walls of the reactor unless a hot walled reactor is used. However, the hot wall reactor causes premature decomposition of the organometallic dimethylcadmium and thus formation of unwanted impurities.

In attempts to minimize these problems, Jackson in U.S. Patent No. 4,439,267 directs a stream of hydrogen carrying vapors of diethyltelluride and dimethylcadmium to a graphite susceptor having two cavities, one containing the CdTe substrate and the other liquid mercury. The susceptor is heated differentially by RF (radio frequency) to allow decomposition of the metal alkyls and vaporization of mercury, respectively, to occur at two different temperatures, such as for example 400°C and 200°C. This process is, however, quite

complex and difficult to control. Furthermore, it does not eliminate condensation of excess mercury vapor elsewhere in cooler areas of the reactor. Hoke, in U.S. Patent No. 4,568,397 discloses a method in which mercury is preheated in a separate reservoir at temperatures greater than 240°C and the mercury vapor is directed to the MOCVD reactor, externally heated to greater than 240°C, and combined with the vapors of the group II organometallics such as dimethylcadmium and group VI organometallic diethyltelluride to form HgCdTe on the heated susceptor containing the substrate. However, this method does not eliminate premature decomposition of dimethylcadmium and interdiffusion is still a problem due to the high temperature (greater than 400°C) required for the decomposition of diethyltelluride. In efforts to minimize, diffusional problems associated with the high temperature growth of tellurides, less stable organotellurides such as diisopropyltelluride [Hoke, Appl. Phys. Lett. 46(4) 398 (1985)] and more recently, di-tert.-butyltelluride [Hoke, Appl. Phys. Lett. 48 (24) 1669 (1986)] have been proposed in efforts to reduce the growth temperatures. However, at these lower temperatures the growth rate for the formation of tellurides was drastically reduced. For example, CdTe an important buffer epitaxial layer for HgCdTe, which formed at the rate of 10 μm/hr. at 370°C using diisopropyltelluride, was grown at only 0.6 μm/hr. at 230°C using tertiary butyl telluride.

In our copending United States Application Serial No. 847,370 filed April 2, 1986 we described the method for low temperature growth of groups II-VI tellurides using 2,5-dihydrotellurophene as the tellurium source. However, a need still exists for organotellurium compounds to provide low temperature epitaxial tellurides at high growth rates.

40

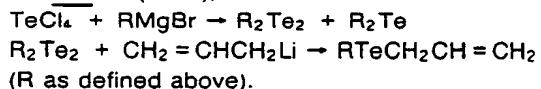
The Invention

This invention deals with the use of certain novel allyltellurides as tellurium sources for the MOCVD epitaxial growth of group II-VI semiconductor compounds. The allyltellurides of this invention in conjunction with dimethylcadmium and/or dimethylmercury provide good quality epitaxial films of CdTe, HgTe, and HgCdTe. The use of dimethylmercury, as the mercury source, eliminates the need for heating the walls of the reactor in order to transport mercury vapor to the substrate, and consequently avoids premature deposition of tellurides and mercury condensation. The allyltellurides of this invention represent a class of

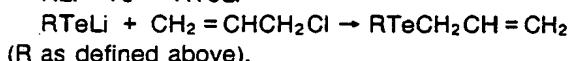
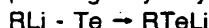
novel compounds characterized by the presence of at least one allyl group and a lower alkyl or allyl group. The alkyl group may be one to four carbon atoms, preferably methyl. This class of compounds is represented by the formula: $RTeCH_2CH=CH_2$ wherein R is alkyl(C₁-C₄) or allyl

Examples of compounds useful in this invention include methyl allyltelluride, ethyl allyltelluride, n-propyl allyltelluride, t-propyl allyltelluride, n-butyl allyltelluride, tert. butyl allyltelluride and diallyltelluride.

The alkyl allyltellurides above may be synthesized by the reaction of a dialkyltelluride and allyl lithium or allyl Grignard reagent according to a general procedure described for the preparation of unsymmetrical dialkyl tellurides, *Organometallics* 2-(2)305 (1983). The starting ditelluride may in turn be prepared by the reaction of tellurium tetrachloride and an alkyl Grignard reagent, *J. Organomet. Chem.* 255 61 (1983).



A most convenient and preferred route for the synthesis of alkyl allyltellurides is the reaction of an alkyl lithium compound first, with tellurium metal to form the lithium allyltelluride intermediate which in turn is reacted with allyl chloride to form the corresponding alkyl allyltelluride.



The diallyltelluride may be prepared by the reaction of allyl bromide or allyl chloride and sodium telluride by a procedure similar to that described for the preparation of dialkyltellurides at *Naturforsch. B. Anorg. Chem.* 33B, 246 (1978) and at *Proceedings, 3rd Int. Symp. Organoselenium and Organotellurium Compounds* p. 391 (1979).



The compounds of this invention may be used as tellurium sources for the preparation of group II-VI epitaxial films such as HgTe, CdTe, PbTe, HgCdTe, CdMnTe and the like. In the practice of this invention, vapors of the appropriate Group II metal such as dimethylmercury and/or dimethylcadmium are directed along with vapors of the allyltelluride derivatives of this invention, with or without premixing, at a crystalline substrate such as cadmium telluride (CdTe), indium phosphide (InP), indium antimonide (InSb), gallium arsenide (GaAs), alumina, sapphire, silicon, zirconia. In some embodiments, the group II element is added as metal vapor, e.g. mercury vapor, by diffusion, e.g., from a pool on the susceptor or by external vaporization followed by transport to the heated

substrate in a carrier gas. Preferably, the substrate is in the form of a wafer which rests on a graphite susceptor heated by a radio frequency, r.f., induction heater. A more detailed description of the apparatus may be found in *J. Electrochem. Soc. Solid State Sci.* Vol. 116, 1725 (1969); *J. Appl. Phys.* Vol. 54, 5087 (1983); *Appl. Phys. Lett.* Vol. 46, 398 (1985), *Handbook on Semiconductors*, Vol. 3, Chapter 5 p. 350 (1980) and U.S. Patents Nos. 4,368,098 and 4,568,397.

Using the method of this invention, epitaxial films of CdTe, HgTe and HgCdTe are successfully grown on CdTe substrate at substrate temperatures 250-350°C. The ratio of group VI organotelluride to group II compound in the gases fed to the reactor can vary widely, but preferably the mole fraction ratio will be at least 1:1. In the case in which elemental mercury is used as the group II compound, the mole fraction ratio may be as low as 0.1. More detailed description of specific embodiments of the invention are described by examples below.

EXAMPLE 1

PREPARATION OF METHYL ALLYLTELLURIDE

In a 1000 ml pressure bottle equipped with a stirrer is added 30.2 g. (0.237 mole) of tellurium and 400 ml tetrahydrofuran under argon atmosphere. The mixture is cooled to -78° with stirring and 175 ml of a 1.7 M ether solution of methyl-lithium (0.296 mole) is added over a 15 minute period and allowed to react for 45 minutes. The reaction mixture is warmed to room temperature and the tetrahydrofuran/ether solvent mixture is evaporated under vacuum.

The residue is cooled to -78° and 250 ml ether is added followed by 22.6 g (0.296 mole) allyl chloride. The reaction mixture is stirred for 18 hours and filtered. To the filtrate is added 200 ml pentane and the ether/pentane solution is washed with five-500 ml portions of deionized water and the solvent layer is separated and subjected to vacuum stripping at room temperature. The residue is distilled under vacuum at 45°/23 mm to give a total of 31.7 g (97.2 %) methyl allyltelluride.

EXAMPLE 2

PREPARATION OF ALKYL ALLYLTELLURIDES

Using the general procedure described in Example 1, ethyl lithium, n-propyl lithium, n-butyl-lithium and t-butyl lithium are reacted, respectively, with tellurium metal to form the corresponding lith-

ium organotellurides. The latter are reacted with allyl chloride to form, respectively, ethyl allyltelluride, n-propyl allyltelluride, n-butyl allyltelluride and t-butyl allyltelluride.

EXAMPLE 3

PREPARATION OF DIALLYL TELLURIDE

Sodium telluride is prepared by the reaction of sodium and tellurium in liquid ammonia. After evaporation of the ammonia, a solvent, for example ether, is added and the slurry is reacted with allyl chloride to give diallyltelluride.

EXAMPLE 4

MOCVD GROWTH OF CdTe

Mixed cool (20°) vapors of dimethylcadmium and methyl allyltelluride (MATE) are introduced into a vertical MOCVD reactor using palladium diffused hydrogen as the carrier gas [a description of the type apparatus that may be used is found in Manasevit U.S. Patent No. 4,368,098]. The mixed vapors are directed to a crystalline cadmium telluride (CdTe) substrate placed on a graphite susceptor which is heated to 290°C by radio frequency (RF) induction. At a flow ratio of hydrogen carrier gas through dimethylcadmium to hydrogen carrier gas through MATE of 0.2, a growth rate of CdTe of approximately 3 $\mu\text{m}/\text{hr}$ per 100 SCCM of hydrogen flow through the MATE bubbler is obtained. Reproducible, temperature independent CdTe growth rates as high as 24 $\mu\text{m}/\text{hr}$ are achieved at or above 290°C.

EXAMPLE 5

MOCVD GROWTH HgTe

Following the general procedure described in Example 4, mixed cool vapors of dimethylmercury and methyl allyltelluride are reacted on a cadmium telluride substrate to form HgTe epitaxial films. Growth rates of 12 $\mu\text{m}/\text{hr}$. are achieved at 325-350°. Mercury telluride epitaxial films are also grown on CdTe substrate by the use of excess mercury vapors instead of dimethylmercury.

EXAMPLE 6

MOCVD GROWTH OF HgCdTe

Following the general procedure described in Example 4, mixed cool vapors of dimethylmercury, dimethylcadmium and methyl allyltelluride are allowed to impinge on indium antimonide substrate to form mercury cadmium telluride [Hg_{1-x}Cd_xTe]. Growth rates of 4 $\mu\text{m}/\text{hr}$. are achieved for x = 0.2-0.3 at 325-350°C.

Claims

1. Organometallic tellurides of the formula:

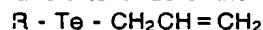


wherein R is alkyl having 1 - 4 carbon atoms, or allyl.

2. A compound defined by Claim 1 wherein R is methyl.

3. A compound defined by Claim 1 wherein R is allyl.

4. In a process for the preparation of group II-VI epitaxial films which comprises directing vapors of at least one group II metal or organometallic compound of a group II metal along with vapors of an organotellurium compound at a crystalline substrate in a MOCVD reactor with at least the substrate heated to temperature sufficient for growth of an epitaxial film of a group II tellurium compound by reaction of said vapors on the substrate, the improvement wherein said organotellurium compound is a telluride of the formula:



wherein R is alkyl having 1 - 4 carbon atoms or allyl.

5. An improved process defined by Claim 4 wherein the substrate is heated to temperature in the range from 250° to 350°.

6. An improved process defined by Claim 4 wherein the mole ratios of the telluride vapor to the group II organometallic vapor fed to the reactor is at least 1:1.

7. A process defined by Claim 4 wherein the organotellurium compound is selected from methyl allyltelluride.

8. An improved process defined by Claim 4 wherein the group II organometallic compound is dimethylmercury or dimethylcadmium or both.

9. An improved process defined by Claim 4 wherein the mole ratios of group II metal vapor to the telluride vapor fed to the reactor is 1:1 to 10:1.

10. An improved process defined by Claim 9 wherein the group II metal vapor is mercury vapor.

11. A process defined by Claim 6 wherein the organotellurium compound is selected from methyl allyltelluride.



EP 88 10 3673

DOCUMENTS CONSIDERED TO BE RELEVANT						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)			
P, X	JOURNAL OF APPLIED PHYSICS, vol. 62, no. 12, 15th December 1987, pages 4929-4931, American Institute of Physics, New York, US; R. KORENSTEIN et al.: "Metalorganic growth of HgTe and CdTe at low temperatures using dialkyltelluride" * Whole article * ----	1-11	C 07 C 165/00 C 30 B 25/02 C 30 B 29/48 C 23 C 16/18			
A	TETRAHEDRON LETTERS, vol. 24, no. 46, 1983, pages 5109-5112, Pergamon Press Ltd., Oxford, GB; A. OSUKA et al.: "Dialkyltelluronium allylide as a novel reagent for synthesis of alpha,beta-unsaturated epoxides" ----					
A	EP-A-0 040 939 (THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY'S GOVERNMENT OF THE UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND) ----					
A, D	APPLIED PHYSICS LETTERS, vol. 46, no. 4, 15th February 1985, pages 398-400, American Institute of Physics, New York, US; W.E. HOKE et al.: "Metalorganic growth of CdTe and HgCdTe epitaxial films at a reduced substrate temperature using diisopropyltelluride" -----		TECHNICAL FIELDS SEARCHED (Int. Cl. 4) C 07 C C 23 C C 30 B			
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Place of search THE HAGUE</td> <td>Date of completion of the search 29-06-1988</td> <td>Examiner COOK S.D.</td> </tr> </table> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>				Place of search THE HAGUE	Date of completion of the search 29-06-1988	Examiner COOK S.D.
Place of search THE HAGUE	Date of completion of the search 29-06-1988	Examiner COOK S.D.				

